

FORM PTO-1390
(REV 12-29-99)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

1-15247

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/763481

INTERNATIONAL APPLICATION NO.
PCT/DE99/02582

INTERNATIONAL FILING DATE
13 August 1999 (13.08.99)

PRIORITY DATE CLAIMED
28 August 1998 (28.08.98)

TITLE OF INVENTION

PROCESS FOR THE PRODUCTION OF AN ELECTROCHROMIC COATING

APPLICANT(S) FOR DO/EO/US

AXEL NOETHE et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☒ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☒ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)), with amended sheets (English translation)

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment, w/Exhibit
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.

16. ☒ Other items or information: Return card;
express mail certificate
Int'l Search Report ISA/210;
Int'l Preliminary Exam Report
w/English translation of
Annexes and amended sheets

"Express Mail" Mailing Label Number EL469909030US

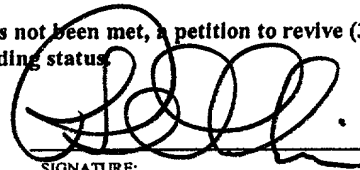
Date of Deposit February 21, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231
Kathleen J. Moore

(typed or printed name)

Kathleen J. Moore

(Signature)

U.S. APPLICATION NO. 09/763481 INTERNATIONAL APPLICATION NO. PCT/DE99/02582		ATTORNEY'S DOCKET NUMBER 1-15247	
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =		CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$ 860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		\$ -	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	13 - 20 =	0	X \$18.00
Independent claims	1 - 3 =	0	X \$80.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00
TOTAL OF ABOVE CALCULATIONS =			\$ 860.00
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).			\$ -
SUBTOTAL =			\$ 860.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			\$ -
TOTAL NATIONAL FEE =			\$ 860.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property			\$ 0
TOTAL FEES ENCLOSED =			\$ 860.00
Amount to be refunded:			\$
charged:			\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ 860.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>13-1816</u> . A duplicate copy of this sheet is enclosed.			
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.			
SEND ALL CORRESPONDENCE TO: MARSHALL & MELHORN, LLC Phillip S. Oberlin Four SeaGate - 8th Floor Toledo, Ohio 43604 Phone: (419) 249-7149 Fax: (419) 249-7151 February 21, 2001		 SIGNATURE: PHILLIP S. OBERLIN NAME 19,066 REGISTRATION NUMBER	

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I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on February 21, 2001 and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Kathleen J. Moore
(Signature of person mailing correspondence)

Kathleen J. Moore
(Typed name of person mailing correspondence)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:]	
AXEL NOETHE and STEFAN MENZEL]	Group Art Unit:
]	
Serial No.]	
Filed:]	Examiner:
]	
Filing Under 35 U.S.C. 371 in]	
the DO/EO/US off PCT/DE99/02582]	
filed 13 August 1999 (13.08.99)]	
]	
For: PROCESS FOR THE PRODUCTION]	Attorney Docket 1-15247
OF AN ELECTROCHROMIC COATING]		

February 21, 2001

Assistant Commissioner for Patents
BOX PCT
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Honorable Sir:

Prior to the first Office Action and before calculating the filing fee, please amend the application being filed concurrently herewith under 35 U.S.C. 371 as follows:

IN THE SPECIFICATION

Page 1, above line 1, insert --TITLE--; line 1, delete "Process for the production of an electrochromic coating" and insert --PROCESS FOR THE PRODUCTION OF AN ELECTROCHROMIC COATING--;

line 2, insert --BACKGROUND OF THE INVENTION--;

line 3, delete "Specification" and insert --1. Field of the Invention--.

Page 2, line 19, insert --2. Description of the Related Art--.

Page 5, line 3, insert the following paragraph:

--WO 96/06203A discloses the manufacture of electrochromic elements by coating with WO_3 , Nb_2O_5 , V_2O_5 , NiO or IrO_2 by reactive sputtering in an atmosphere of oxygen and argon.--

line 19, insert --SUMMARY OF THE INVENTION--.

Page 10, line 14, insert --BRIEF DESCRIPTION OF THE DRAWING--;

line 17, delete "The electrochromic";

between lines 17 and 18, insert --DESCRIPTION OF THE PREFERRED EMBODIMENTS--;

line 18, before "element" insert --The electrochromic--.

IN THE CLAIMS

Please amend the claims as follows:

1. (Amended) [Process] A process for the production of an electrochromic coating on a substrate by cathode sputtering of a target in a coating atmosphere containing a noble gas, in particular argon, and hydrogen ions, [characterized in that] wherein at least one gaseous hydrocarbon is added to the coating atmosphere.
2. (Amended) [Process] A process according to claim 1, [characterized in that] wherein said at least one gaseous [saturated] hydrocarbon is a saturated hydrocarbon [added to the coating atmosphere].
3. [Process] A process according to claim 2, [characterized in that] wherein [methane is used as] said saturated hydrocarbon is methane.
4. [Process] A process according to claim 2, [characterized in that] wherein said saturated hydrocarbon is selected from the group consisting of ethane, propane [or] and butane [is used as hydrocarbon].

5. [Process] A process according to [one of claims 1 to 4, characterized in that] claim 1, wherein oxygen is additionally added to the coating atmosphere.
6. (Amended) [Process] A process according to claim 5, [characterized in that] wherein the volumetric ratio of added hydrocarbon to added oxygen is in the range 3:1 to 1:3, in particular approximately 1:1.
7. (Amended) [Process] A process according to claim 5 [or 6], [characterized in that] wherein the volumetric ratio of noble gas, in particular argon, to oxygen is in the range of 3:1 to 1:3, in particular approximately 1:1.
8. (Amended) [Process] A process according to [one of claims 1 to 7, characterized in that] claim 1, wherein operation takes place at a total pressure of the coating atmosphere of $0.3 \cdot 10^{-2}$ mbar to 10^{-1} mbar, in particular of $1 \cdot 10^{-2}$ mbar to $4 \cdot 10^{-2}$ mbar.
9. (Amended) [Process] A process according to [one of claims 1 to 8, characterized in that] claim 1, wherein a target consisting of tungsten or of a tungsten alloy is used.

10. (Amended) [Process] A process according to [one of claims 1 to 9, characterized in that] claim 1, wherein a target containing molybdenum, titanium, cerium, vanadium and/or zirconium is used.
11. (Amended) [Process] A process according to [one of claims 1 to 10, characterized in that] claim 1, wherein the electrochromic coating (16, 20) is applied with a thickness in the range of 50 nm to 500 nm.
12. (Amended) [Electrochromic] An electrochromic element with at least one electrochromic coating (16, 20) which has been produced in accordance with the [according to a] process [according to one of the foregoing claims] of claim 1.
13. (Amended) [Electrochromic] An electrochromic element according to claim 12, [characterized in that] wherein Li^+ ions are used as charge carriers.

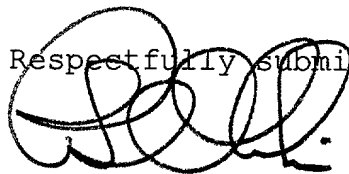
REMARKS

Applicants have amended the application to eliminate multiple dependencies, to incorporate the amendment filed in the European Patent Office on June 29, 2000, in PCT/DE99/02582, the priority of which is claimed (copy attached hereto as Exhibit A), and to adapt the specification, claims and abstract to U.S. patent practice.

Original claims 1-13 have been amended and are currently pending in the present application. No new matter has been added by any of the above amendments.

Favorable consideration of the application as amended is respectfully requested.

Respectfully submitted,



Phillip S. Oberlin
Registration No. 19,066

ATTORNEYS
MARSHALL & MELHORN, LLC
Four SeaGate - 8th Floor
Toledo, Ohio 43604
Phone: (419) 249-7149
Fax: (419) 249-7151

1. Section V:

The documents of the International Search Report are considered relevant as indicated below:

D1= WO 96 06203 A (OPTICAL COATING LABORATORY INC), February 29, 1996 (1996-02-29)

D2 = DE 43 05 414 A (LINDE AG) August 25, 1994 (1994-08-25)

1.1 The current Claims 12-13 are interpreted "per se" as product claims. In other words, the objects of these claims (electrochromic elements) must be novel and inventive, regardless of their intended use or their manufacturing process. Therefore any document that discloses an object like the one claimed must be considered adverse to the novelty of said object, even if said object was manufactured using a different method or process or is used for a different purpose.

1.2 Document D1 discloses the manufacture of electrochromic elements (see Figures 1A-1B; Page 1, Line 29 to page 3, Line 5) by coating with WO_3 , Nb_2O_5 , V_2O_5 , NiO or IrO_2 etc. by reactive sputtering in an atmosphere of oxygen and argon (See Claims 1-13; Page 10, Line 30 to Page 14, Column 16; Examples 1-4). Thus the electrochromic elements manufactured according to D1 also do not have any carbon which, according to this application (See Page 5, second full paragraph) is present in a few atomic per cent.

The addition of hydrocarbons to this sputtering atmosphere is neither mentioned in D1 nor can it be inferred, although the depositing of other defined layers such as nitrides, oxynitrides, carbides etc. is mentioned (See Page 17, Line 20 to Page 18, Line 21). In particular, there is no mention in D1 that such an addition during the deposit of the electrochromic layer leads to a reduction of the reactive charge.

1.3 Document D2 discloses, very generally, a method for coating a substrate (in particular glass) with a metal oxide coating, in particular tin oxide, by means of sputtering in an atmosphere with a balanced basic gas mixture that has an oxidizing and reducing effect, and consists of at least 20 vol.% oxygen, hydrogen and a gaseous hydrocarbon or halogenated

hydrocarbon, optionally with 5-40 vol.% argon (See Claims 1-2). This gas mixture prevents the accretion of the target with oxides (see Column 1, Lines 13-37; Column 2, Lines 40-43).

The manufacture of electrochromic coatings or of electrochromic elements is nowhere mentioned in D2. Document D2 can therefore not be combined with D1, not even by way of inference, because D1 addresses an entirely different objective.

1.4 The remarks presented above show that Claims 1-13 satisfy the requirements of Article 33(2) and (3) PCT. The industrial applicability of the claimed method and of the electrochromic elements is obvious.

Amended Sheet 3 contains the following text. The new text is underlined:

... increases drastically. A lengthy conditioning process, however, renders production more costly and is thus undesirable. In addition, Electrochromic coatings produced according to the prior art frequently possess insufficient storage capacity or inadequate coloring efficiency (ratio of transmission range to intercalated charge per unit of area).

WO 96/06203A discloses the manufacture of electrochromic elements by coating with WO_3 , Nb_2O_5 , V_2O_5 , NiO or IrO_2 by reactive sputtering in an atmosphere of oxygen and argon.

A process according to the preamble of Claim 1 is known from GB 2 086 601 A. According to this publication ...oxygen and hydrogen vapor are added to the coating atmosphere, in order to produce electrochromic hydroxide coatings from metal targets. As a coating process clearly preferable to cathode sputtering with a coating atmosphere containing water vapor, reactive ion plating with the addition of water vapor is employed. The electrochromic coatings produced in this way are used for the production of electrochromic displays where H^+ ions are used as charge carriers. In a large-scale industrial sputtering process, the addition of water vapor to the coating atmosphere can only be controlled with difficulty and leads to significant lack of uniformity in the coating properties and in the distribution of coating thickness.

The object of the invention is to provide a process with which electrochromic coatings can be produced by cathode sputtering with at all events less positive or even negative blind charge. With the process, it should in addition be possible to produce electrochromic coatings with higher storage capacity (absorption capacity) for positively charged ions, in particular W^+ ions or Li^+ ions. The process should be easier to control than cathode sputtering in a coating atmosphere with addition of water vapor.

Amended Sheet 3a contains the following text:

To achieve this object, the invention proposes that at least one gaseous hydrocarbon be added to the coating atmosphere. Especially suitable are the saturated hydrocarbons, and preferably methane. This gaseous saturated hydrocarbon is characterized by an especially high proportion of hydrogen to carbon per molecule. It has been found that the desired effect of the addition to the coating atmosphere according to the invention is best achieved if the ratio of hydrogen to carbon in the molecule of the hydrocarbon is high, as with excessive carbon content of the molecule, excessive carbon is incorporated in the coatings, as a result of which the electrochromic properties can deteriorate. In addition, it is possible, with a ...

Process for the production of an electrochromic coating

Specification

The invention relates to a process for the production of an electrochromic coating on a substrate by cathode sputtering of a target in a coating atmosphere containing hydrogen ions, as well as to an electrochromic element with at least one such coating.

Designated as electrochromic coatings are coatings which are capable of reversibly absorbing (intercalating) and again emitting (decalating) cations, in particular H^+ ions or Li^+ ions, their optical properties generally changing in this process. They consist principally of metal oxides or mixed metal oxides. Electrochromic materials include anodically and cathodically colourable materials, as well as pure ion-storage materials, whose optical properties depend only slightly or not at all on the amount of the intercalated cations.

Electrochromic elements are increasingly gaining interest as so-called "intelligent windows" whose light transmission or other optical properties can be selectively influenced by temporary application of an electrical voltage. Such electrochromic elements generally consist of substrates, in

particular of transparent glass or plastic, provided on one side with conductive coatings, an electrochromic coating being arranged in each case on the conductive coatings.

The substrates coated in this way are connected to one another by interposing an electrolyte (ion conductor).

By application of a voltage to the conductive coatings, cations located in the electrochromic element, generally H^+ or Li^+ ions, are intercalated into one of the

electrochromic coatings (the electrochromic coating in the actual sense of the term), as a result of which its optical properties change in the desired sense. The other electrochromic coating, which usually consists of a different material as the first-mentioned electrochromic coating, frequently acts as an ion storage coating not significantly altering its optical properties which, on application of a voltage of opposite sign, is capable of absorbing the cations now decalated from the other electrochromic coating.

An electrochromic element of this type can be found for example in publications DE 197 06 918 A1, EP 0 683 215 A1, WO 95/31746 A1. As material for the electrochromic coating in the actual sense, which significantly alters its optical properties during intercalation and decalation of cations, tungsten oxide (WO_x) has in practice been found

satisfactory, as mixed oxide or interspersed with doping additives. As material for electrochromic coatings which are used as ion storage coatings, mixed oxides, such as cerium-titanium oxide or vanadium-titanium oxide, are known inter alia.

For the production of such electrochromic coatings, a series of different coating processes are known, these including for example CVD or sol-gel processes, as well as physical processes, such as various vacuum metallizing processes, ion plating or cathode sputtering. For large-area electrochromic elements, cathode sputtering is primarily involved for reasons of cost for the production of the individual coatings, and here in particular reactive DC or medium-frequency magnetron cathode sputtering of metal or semi-conductive targets.

Electrochromic coatings are not generally fully functional directly after their production or after assembly of all components to form an electrochromic element. On the contrary, they must be conditioned, which means that the electrochromic coatings or the electrochromic element are cyclically charged and discharged until the desired maximum transmission range is reached. By transmission range is meant the transmission difference between the coloured and

bleached state of the electrochromic coating or of the electrochromic element. Only subsequently is the electrochromic element usable over a long period of time and can be switched between defined initial and final states. If one conditions electrochromic coatings produced according to the state of the art with the aid of a liquid electrolyte, such as propylene carbonate with Li salt dissolved in it and a standard counter-electrode, one will find that during the initial charge/discharge cycle a significant difference occurs between the intercalated and the deintercalated charge. The so-called "blind charge" (unit: mC/cm^2) consists of positive charge carriers, for example H^+ ions or Li^+ ions which remain irreversibly in the electrochromic coating after the initial charge cycle and thus permanently reduce the number of the charge carriers available for the electrochromic element. It has been observed in the process that, with an increasing positive blind charge, the duration of the necessary conditioning of the electrochromic element increases drastically. A lengthy conditioning process however renders production more costly and is thus undesirable. In addition, electrochromic coatings produced according to the state of the art frequently possess insufficient storage capacity or inadequate colouring efficiency (ratio of

transmission range to intercalated charge per unit of area).

A process according to the preamble of claim 1 is known from GB 2 086 601 A. According to this publication, oxygen and hydrogen vapour are added to the coating atmosphere, in order to produce electrochromic hydroxide coatings from metal targets. As a coating process clearly preferable to cathode sputtering with a coating atmosphere containing water vapour, reactive ion plating with the addition of water vapour is employed. The electrochromic coatings produced in this way are used for the production of electrochromic displays where H^+ ions are used as charge carriers. In a large-scale industrial sputtering process, the addition of water vapour to the coating atmosphere can only be controlled with difficulty and leads to significant lack of uniformity in the coating properties and in the distribution of coating thickness.

The object of the invention is to provide a process with which electrochromic coatings can be produced by cathode sputtering with at all events less positive or even negative blind charge. With the process, it should in addition be possible to produce electrochromic coatings with higher storage capacity (absorption capacity) for

positively charged ions, in particular H^+ ions or Li^+ ions. The process should be easier to control than cathode sputtering in a coating atmosphere with addition of water vapour.

5

To achieve this object, the invention proposes that at least one gaseous hydrocarbon be added to the coating atmosphere. Especially suitable are the saturated hydrocarbons, and preferably methane. This gaseous saturated hydrocarbon is characterized by an especially high proportion of hydrogen to carbon per molecule. It has been found that the desired effects of the addition to the coating atmosphere according to the invention is best achieved if the ratio of hydrogen to carbon in the molecule of the hydrocarbon is high, as with excessive carbon content of the molecule, excessive carbon is incorporated in the coatings, as a result of which the electrochromic properties can deteriorate. In addition, it is possible with a high H:C ratio, to set the overall pressure of the coating atmosphere comparatively low and thus the coating rate relatively high. Other suitable gases are primarily ethane, propane or butane. Of course, a noble gas is also added to the coating atmosphere at all times - this is normally argon - this being required as non-reactive gas for target sputtering.

20

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Especially with the reactive cathode sputtering of metal or semi-conductive targets specially preferred within the scope of the invention, oxygen is additionally added to the coating atmosphere. The volume ratio of added hydrocarbon to added oxygen is preferably set in the range of 3:1 to 1:3, especially at approximately 1:1. With lower levels of hydrocarbons, the desired effects can no longer be achieved to a sufficient extent, whilst with higher levels of hydrocarbons, the electrochromic properties of the coatings deteriorate or the sputtering process is more difficult to control.

It is especially preferable during cathode sputtering for the volume ratio of argon to oxygen to be in the range of 3:1 to 1:3, in particular at approximately 1:1.

The stated ratios are set by means of corresponding adjustments of the metering valves for the gases in question. A ratio of 1:1 corresponds for example to the same setting of the gas flow rate for both gases.

A sufficiently high coating rate, as well as especially good coating properties, are achieved if one employs an

overall gas pressure of the coating atmosphere of $0.3 \cdot 10^{-2}$ mbar to 10^{-1} mbar, especially of $1 \cdot 10^{-2}$ mbar to $4 \cdot 10^{-2}$ mbar.

5 The process according to the invention is especially suitable for the production of electrochromic coatings with tungsten oxide base, for which then a target of tungsten or tungsten alloy is employed. Another application provides for the use of a target containing molybdenum, titanium, cerium, vanadium and/or zirconium.

The process is preferably carried out such that electrochromic coatings with a thickness in the range of 50 nm to 500 nm are obtained. Normally, thinner coatings no longer possess an adequate transmission range or an adequate storage capacity for charge carriers. Thicker coatings provide no significant advantages and can no longer be produced cost-effectively in uniform quality.

20 With electrochromic coatings produced according to the invention, it is possible to produce electrochromic elements with high colouring efficiency (high transmission range per intercalated charge per unit of area). In addition, in some cases, an increased intercalation rate of H^+ ions and Li^+ ions could also be observed in

electrochromic coatings produced in this way, so that it was possible to produce electrochromic elements with higher operating rate than with conventionally applied electrochromic coatings. Above all, the time required for conditioning the electrochromic element can be significantly reduced by the use of the invention. It was also found that electrochromic coatings produced according to the invention possess higher thermal resistance in comparison with coatings having been produced without addition to the coating atmosphere according to the invention. It is supposed that at least part of these effects is based on incorporation of carbon atoms in the matrix of the electrochromic material. In fact, it was found for coatings produced according to the invention by thermodesorption analysis that they contained carbon in the order of magnitude of some atomic percent. The invention has proved especially satisfactory in the production of electrochromic elements with Li^+ ions as charge carriers, in particular with a polymer electrolyte according to

WO 95/31746 A1.

The invention can be applied to special advantage during reactive DC or medium frequency sputtering of metal or semi-conductive targets in a coating atmosphere containing argon, oxygen and hydrocarbon(s). Basically however, it

can also be used in HF sputtering of oxidic targets, where of course the oxygen content of the coating atmosphere will normally be lower than is the case with reactive cathode sputtering. Electrochromic coatings produced according to the invention are used to special advantage for production of hermetically sealed electrochromic elements, where the number of charge carriers available for charge transfer is limited. Here, the invention is not confined to electrochromic elements with Li^+ ions as charge carriers. On the contrary, it is also possible to use H^+ ions or other positively charged ions.

The invention is explained below with the aid of examples.

The single Figure illustrates in schematic form an electrochromic element with an electrochromic coating produced according to the invention. The electrochromic element consists of a first glass pane 10 and a second glass pane 12, both of which are essentially flat and have dimensions of for example approximately $40 \cdot 80 \text{ cm}^2$. The first glass pane 10 bears on its surface facing downwards in the drawing a first conductive layer 14, this being for example an indium-tin oxide (ITO) coating with a thickness of 300 nm. Onto the first conductive layer 14 is applied an electrochromic coating 16 of WO_x by a process according

to the invention. The second glass pane 12 bears on its side facing towards the first glass pane 10 a second conducting layer 18, which for example also consists of indium-tin oxide, with a thickness of 300 nm. Adjacent to the second conductive layer 18, on the side opposite to the second glass pane 12 is an ion storage coating 20 of $\text{Ce}_x\text{Ti}_y\text{O}_z$ with a thickness of 280 nm, which has preferably been produced by a process according to the invention. The two glass panes 10, 12 provided with coatings described above are bonded to one another in the manner of a laminated pane by an ion conduction layer 22, which in the case of the example illustrated has a thickness of 1 mm and consists of a plastic matrix with embedded salts (polymer electrolyte). An edge seal 24 seals the ion conduction layer 22 towards the outside of the element; through it are also led out in customary fashion the contacts 26, 28 which are connected to the electrode layers 14, 18.

The examples below illustrate with the aid of the coating of specimen glass panes according to a known process and according to processes according to the present invention how blind charge and conditioning time are reduced in the presence of hydrocarbons in the coating atmosphere.

Examples 1 - 4

Glass panes measuring $10 \cdot 10 \text{ cm}^2$ with a thickness of 2 mm provided with indium-tin oxide (ITO) as conductive layer with a surface resistance of 10Ω were coated in a DC magnetron cathode sputtering system with WO_x corresponding to Column 2 of Table 1. The composition of the coating atmosphere in each case is stated in Columns 3 - 7. The blind charge has been determined subsequent to coating production by the coated pane being immersed in a liquid electrolyte (polypropylene carbonate with Li^+ salt) and being subjected to a charge/discharge cycle, where the blind charge is determined as difference of the charge per unit area which had flowed in each case. The conditioning time was determined on complete electrochromic elements with the structure: glass / ITO conductive layer / WO_x electrode / polymer electrolyte / Ce-Ti oxide counter-electrode / ITO conductive layer / glass.

Table 1

Ex. No.	Thickness [nm]	Relative Volume Parts Ar	Relative Volume Parts O ₂	Relative Volume Parts HC	HC	Total pressure [10 ⁻² mbar]	Blind charge [mC/cm ²]	Cond. time [h]
1	255	4	3	--	--	1.4	10.7	60
2	260	2	2	1	methane	2.5	3.2	20
3	255	2	2	2	methane	3.3	-0.3	1
4	270	2	2	2	ethane	3.8	0.8	4

It becomes clearly recognizable that the blind charge, and thus the conditioning time, is significantly reduced due to the addition of a hydrocarbon gas according to the invention. The coating process took place in comparably stable fashion. No undesirable contamination of the coating apparatus was observed.

Additional trials not described here evidenced a reduced blind charge and overall improved coating properties also with ion storage coatings such as cerium-titanium oxide or titanium-vanadium oxide.

Of course, the invention is applicable to electrochromic elements other than those described as examples. Thus, materials other than ITO, for example SnO₂ doped with fluorine or antimony, can be employed for the conductive layers. It is also possible to use other electrolytes in

place of the preferably employed polymer electrolytes according to WO 95/31746 A1. The advantages of the invention are of course to be found above all with hermetically sealed electrochromic elements with a limited quantity of charge carriers. It can also however be employed to advantage in the case of electrochromic elements which are saturated or even supersaturated with charge carriers prior to assembly.

The features disclosed in the foregoing description, in the claims and/or in the accompanying drawing may, both separately and in any combination thereof, be relevant for realizing the invention.

Claims

1. Process for the production of an electrochromic coating on a substrate by cathode sputtering of a target in a coating atmosphere containing a noble gas, in particular argon, and hydrogen ions, characterized in that at least one gaseous hydrocarbon is added to the coating atmosphere.
2. Process according to claim 1, characterized in that at least one gaseous saturated hydrocarbon is added to the coating atmosphere.
3. Process according to claim 2, characterized in that methane is used as hydrocarbon.
4. Process according to claim 2, characterized in that ethane, propane or butane is used as hydrocarbon.
5. Process according to one of claims 1 to 4, characterized in that oxygen is additionally added to the coating atmosphere.

6. Process according to claim 5, characterized in that the volumetric ratio of added hydrocarbon to added oxygen is in the range 3:1 to 1:3, in particular approximately 1:1.

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7. Process according to claim 5 or 6, characterized in that the volumetric ratio of noble gas, in particular argon, to oxygen is in the range of 3:1 to 1:3, in particular approximately 1:1.

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8. Process according to one of claims 1 to 7, characterized in that operation takes place at a total pressure of the coating atmosphere of $0.3 \cdot 10^{-2}$ mbar to 10^{-1} mbar, in particular of $1 \cdot 10^{-2}$ mbar to $4 \cdot 10^{-2}$ mbar.

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9. Process according to one of claims 1 to 8, characterized in that a target consisting of tungsten or of a tungsten alloy is used.

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10. Process according to one of claims 1 to 9, characterized in that a target containing molybdenum, titanium, cerium, vanadium and/or zirconium is used.

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11. Process according to one of claims 1 to 10,
characterized in that the electrochromic coating
(16, 20) is applied with a thickness in the range of
50 nm to 500 nm.

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12. Electrochromic element with at least one
electrochromic coating (16, 20) which has been
produced according to a process according to one of
the foregoing claims.

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13. Electrochromic element according to claim 12,
characterized in that Li^+ ions are used as charge
carriers.

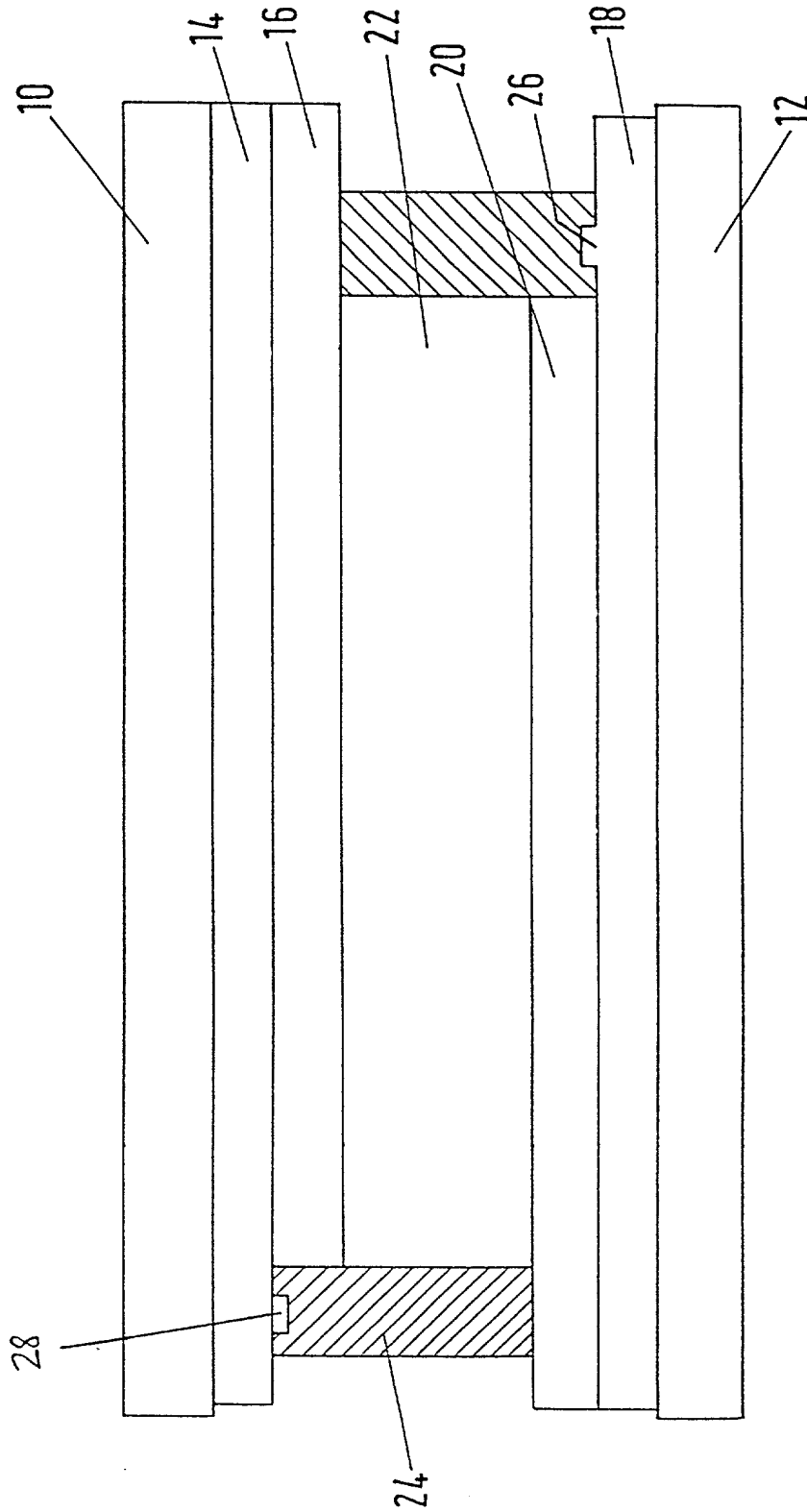
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Abstract

The invention relates to a method for producing an electrochromic layer on a substrate by cathodic sputtering of a target in a coating atmosphere containing an inert gas, especially argon, and hydrogen ions. The method is characterized in that at least one gaseous hydrocarbon is added to the coating atmosphere. The invention also relates to an electrochromic element with at least one electrochromic layer produced according to the inventive method.



COMBINED DECLARATION AND POWER OF ATTORNEY
IN ORIGINAL APPLICATION

ATTORNEY DOCKET
NO. 1-15247

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name,

I believe that I am the original, first, and sole inventor (if only one name is listed below) or an original, first, and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
PROCESS FOR THE PRODUCTION OF AN ELECTROCHROMIC COATING

the specification of which

_____ is attached hereto and which is a filing under
35 USC 371 off PCT International Application No.
PCT/DE99/02582 filed August 13, 1999.

X was filed on _____ as U.S. Serial
No. 09/763,481 under 35 USC 371 off PCT
International Application No. PCT/DE99/02582
filed August 13, 1999 and was amended on
_____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

X and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent; and

_____ if this is a continuation-in-part application, information that occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application, in accordance with 37 CFR 1.63(e); and

_____ in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 CFR 1.98.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
<u>198 39 299.0</u>	<u>Germany</u>	<u>28 August 1998</u>	<u>X</u>	
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Appln. Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
(Appln. Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

If foreign agent is involved, the undersigned hereby authorizes the U.S. attorney or agent named herein to accept and follow instructions from Boehmert & Boehmert (foreign agent) as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney or agent and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorney or agent named herein will be so notified by the undersigned.

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith with full power of substitution and revocation: D. Edward Dolgorukov, Reg. No. 26,266; Phillip S. Oberlin, Reg. No. 19,066; Donald A. Schurr, Reg. No. 34,247; Mark A. Hixon, Reg. No. 44,766; Stephen P. Evans, Reg. No. 47,281; and

Angelica M. Colwell, Reg. No. 46,637, all of the law firm of Marshall & Melhorn, LLC, Four SeaGate - 8th Floor, Toledo, Ohio 43604. Address all telephone calls to Phillip S. Oberlin at telephone number (419) 249-7149. Address all correspondence to MARSHALL & MELHORN, LLC, Four SeaGate - 8th Floor, Toledo, Ohio 43604, Attention: Phillip S. Oberlin.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-0 Full name of sole or first inventor AXEL NOETHE

Inventor's signature *axel noethe* Date 9.4.01
(April 9, 2001)

Residence Amtsstrasse 72, D-44575 Castrop-Rauxel, Germany DEX.

Citizenship Germany / Post Office Address same as above

2-0 Full name of second joint inventor, if any STEFAN MENZEL

Second Inventor's signature *Stefan Menzel* Date 04.04.01
(April 4, 2001)

Residence Koehlerweg 7b, D-93437 Furth im Wald, Germany DEX

Citizenship Germany / Post Office Address same as above

Full name of third joint inventor, if any _____

Third Inventor's signature _____ Date _____

Residence _____

Citizenship _____ Post Office Address _____